

Nano structural features in rare earth doped CeO₂ electrolytes for Solid Oxide Fuel Cells application

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Doped ceria (CeO₂) compounds are fluorite type oxides which show oxide ionic conductivity higher than yttria stabilized zirconia, in oxidizing atmosphere. As a consequence of this, considerable interest has been shown in application of these materials for 'low' or 'intermediate' temperature operation of solid oxide fuel cells (SOFCs). In this study, the authors prepared rare earth (M=Y, Sm and Gd) doped CeO₂ specimens using co-precipitation method, in order to examine the influence of nano-structural feature on electrolytic properties in the sintered bodies. And the relationship between the microstructural feature in nano-scale and the conducting property in those electrolytes were examined. The results give us message that the conducting property in rare earth doped CeO₂ was strongly influenced by the size of coherent micro-domain with ordered structure. Therefore, the author concluded that control of domain size is a key for development of doped CeO₂ electrolytes.

Key words: nano-size micro-domain, doped CeO₂, diffuse scattering, coherent micro-domain, segregation of dopant

1. INTRODUCTION

Oxide ion conductors are used in a variety of oxygen sensors¹, solid oxide electrochemical cells (SOECs) such as membrane reactor² and solid oxide fuel cells (SOFCs)³. In these applications, SOFCs are being especially developed as a clean and efficient power source for generating electricity from a variety of fuels. It is an increasingly attractive prospect. The high quality electrolyte will decrease the operation temperature of the cells, and contribute to a development of portable SOFCs. Yttria stabilized zirconia (YSZ) is the most common electrolyte used in such cells. However, the oxide ionic conductivity of YSZ is unsatisfactory level for the electrolyte of SOFCs in 'low' (500 - 650°C) or 'intermediate' (650 - 800°C) temperature operation.

Accordingly, it is very important that high quality electrolyte with higher oxide ionic conductivity than that of YSZ is identified.

On the other hand, CeO₂ doped with oxides of di- or trivalent metals possess higher oxide ionic conductivity than that of YSZ electrolyte. At high oxygen partial pressures, these CeO₂ based oxides show high oxide ionic conductivity. At low oxygen partial pressures associated with anodic conditions, however, the Ce⁴⁺ ion can be partially reduced to Ce³⁺ ion. The oxide ionic conductivity of doped CeO₂ in reducing atmosphere is not satisfactory level. In order to overcome this problem and improve the conductivity, a design of nano-structure in doped CeO₂ electrolytes is required. Moreover, true microstructures in prepared specimens should be examined at atomic scale to

establish the conduction mechanism.

Recently, rare earth doped CeO₂ electrolytes such as Y doped CeO₂, Gd doped CeO₂, Sm doped CeO₂ and so on are attracted much attention from the viewpoint of application in SOFCs^{4,5}. It has been considered that these doped CeO₂ electrolytes exhibited low activation energy and high conductivity due to small association enthalpy between dopant cation and oxygen vacancy in fluorite lattice. Since doped CeO₂ is one of the promising solid electrolytes in SOFCs for low or intermediate temperature operation, the scrutiny of the relationship between the microstructural feature and the conducting property in these electrolytes is required.

2. EXPERIMENTAL PROCEDURE

2.1. Preparation of Powder and Sintered body

The starting materials were commercial Ce(NO₃)₃·6H₂O powder and rare earth (i.e. Sm, Gd, and Y) nitrate powders. Each powder was dissolved in distilled water, and the solutions were mixed in order to prepare the fixed composition. Ammonium carbonate as the precipitant was dropped into the mixed solution for precipitation. The precipitation was dried under N₂ gas flow and calcined at 700°C to prepare the solid solution. These samples were molded and subjected to a rubber press in order to obtain a green body. Sintering temperature was 1500 to 1600°C and sintering time was 4h in each case.

2.2. Sample Characterization and Conductivity Measurement

The crystal phases of the specimens were identified using X-ray diffraction and selected area electron diffraction pattern of transmission electron microscopy (TEM). TEM observation was performed with gun voltages of 400 and 200keV (JEOL 4010 and 2010).

Electrical conductivity of the sintered specimens was measured by dc three-point measurements from 400° to 700°C in air. The activation energy was

calculated using the data of conductivity at the temperature ranging from 400° to 700°C.

3. RESULTS AND DISCUSSION

Figure 1 presents the Gd content dependence of conducting properties in the Gd doped CeO₂ electrolytes. The activation energy of Gd doped CeO₂ electrolytes was minimized at the composition around $x=0.15$ in Gd_{*x*}Ce_{1-*x*}O₂ system. These results indicates that mobility of oxide ion maximized at the composition around $x=0.15$ in Gd_{*x*}Ce_{1-*x*}O₂ system. The author

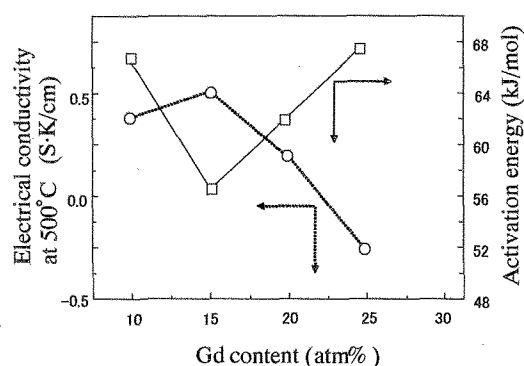


Fig.1 Gd content dependence of conductivity (500°C) and activation energy in Gd doped CeO₂ sintered bodies.

concluded that the electrolytic properties strongly depend on the micro-structure in the sintered body. To conclude why the conductivity and activation energy in Gd doped CeO₂ electrolytes has optimum value in Gd doped CeO₂ electrolytes, the crystal phases and micro-structures in the

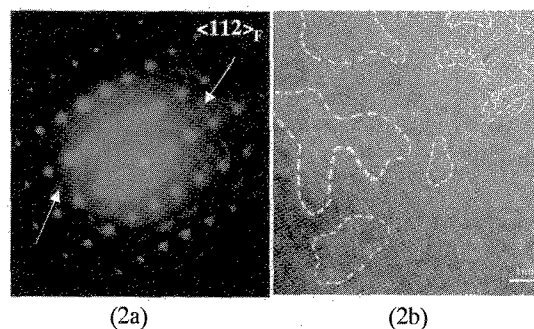


Fig. 2a) Selected area electron diffraction pattern $\langle 112 \rangle_F$ and 2b) high resolution image $\langle 110 \rangle_F$ recorded from Gd_{0.15}Ce_{0.85}O_{1.925} sintered body. Dashed area indicates micro-domain. White arrow indicates extra spot.

sintered bodies were examined.

Figures 2a and 2b display the selected area electron diffraction pattern and high resolution image recorded from $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ sintered body.

As shown in Fig.2a, this specimen has a big diffuse scatter in the background of electron diffraction pattern. This result indicates that coherent micro-domain exists in the fluorite lattice. And Fig.2b indicates that the size of micro-domain is approximately 7nm units or less in the grain of the sintered body. To compare the microstructural features in other specimens, the electron diffraction pattern and high resolution image were observed in $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body.

Figures 3a and 3b show the selected area electron diffraction pattern and high resolution image recorded from $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body.

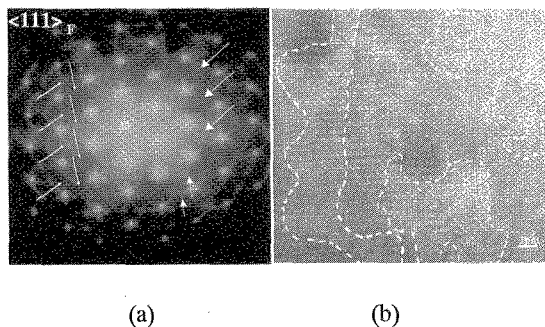


Fig. 3a) Selected area diffraction pattern $\langle 111 \rangle_F$ and 3b) high resolution image $\langle 110 \rangle_F$ recorded from $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered body. Dashed area indicates micro-domain. White arrow indicates extra spot.

A significant diffuse scatter and extra spots were recorded in the electron diffraction pattern. As Fig.3b indicates, the size of micro-domain is over 10 nm unit. Several micro-domains combined each other and formed continues micro-domains. The micro-domain size in $\text{Gd}_{0.15}\text{Ce}_{0.85}\text{O}_{1.925}$ and $\text{Gd}_{0.1}\text{Ce}_{0.9}\text{O}_{1.95}$ sintered bodies was much smaller than that of $\text{Gd}_{0.20}\text{Ce}_{0.80}\text{O}_{1.90}$ and $\text{Gd}_{0.25}\text{Ce}_{0.75}\text{O}_{1.875}$ sintered bodies. The micro-domain with ordered structure would lower the mobility of oxide ion

and the electrolytic properties in the specimens. In addition, the author concludes that the structure of micro-domain is b-type rare earth structure as same as Gd_2O_3 .

Same relation between conducting properties and microstructural features was observed in Y doped CeO_2 and Sm doped CeO_2 systems. Figure 4 displays the selected area electron diffraction pattern recorded from $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ sintered body.

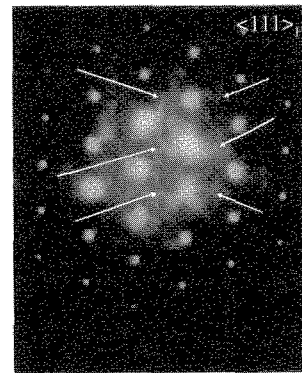


Fig.4 Selected area diffraction pattern $\langle 111 \rangle_F$ recorded from $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ sintered body. Dashed area indicates micro-domain. White arrow indicates extra spot.

This figure indicated that coherent micro-domain with ordered structure existed in $\text{Sm}_{0.2}\text{Ce}_{0.8}\text{O}_{1.9}$ sintered body. From analysis of high resolution image recorded from this specimen, the size of micro-domain was over 10nm unit. Therefore, we conclude that rare earth doped CeO_2 electrolytes have micro-domain with ordered structure. A control of micro-domain size would be a key for development of high quality rare earth doped CeO_2 electrolytes.

In order to minimize the size of micro-domain in the sintered body, round shape powder was prepared using co-precipitation method. The particle morphology of doped CeO_2 powder was changed by the concentration ratio (R) between dopant and precipitant. The round shape Sm doped CeO_2 powder was prepared at $R=10$. Figure 5 presents TEM photograph of round shape Sm

doped CeO₂ particles.

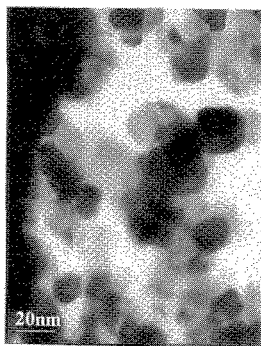


Fig.5 TEM photograph of round shape particles.

The average particle size of this round shape particle was approximately 20 nm unit. The dense sintered was prepared using this round shape particles.

Figure 6 shows high resolution image recorded from Sm_{0.2}Ce_{0.8}O_{1.9} sintered body which is made from round shape particles.



Fig. 6 High resolution image recorded from round specimen.

The sintered bodies which were made from round shape particles had small micro-domains in the grain. In addition, this specimen had low activation energy and high conductivity as compared with previous reported one. The author concludes that the micro-domain is formed to minimize lattice distortion in the grain. The lattice distortion would be minimized in the sintered body which was made from round shape particles. It is because the compact body of round shape particles has homogeneous grain boundary. The lattice distortion would be minimized

in the specimen during sintering. A control of powder morphology is important to minimize the domain size in the sintered body. The author concludes that the subtle change of microstructure at atom scale gives electrolytic properties in doped CeO₂ electrolyte a big change.

4. CONCLUSIONS

Rare earth doped CeO₂ electrolytes were prepared in order to examine the influence of nano-structural feature on conducting properties in doped CeO₂. The main results are summarized as follows:

- (1) The big diffuse scatter and small extra spots were observed in the selected area electron diffraction patterns recorded from rare earth doped CeO₂ sintered bodies. This result suggests that the coherent micro-domain with ordered structure exists in the grain of sintered bodies.
- (2) The big micro-domain lowered the conducting properties in doped CeO₂ electrolytes.
- (3) The size of micro-domain in doped CeO₂ sintered body could be minimized using round shape doped CeO₂ nano-powders.

We conclude that all rare earth doped CeO₂ electrolytes have coherent micro-domain with ordered structure. In order to improve the conducting property in doped CeO₂, the micro-domain size should be minimized.

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